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Claudete Gindri Ramos
Universidad de la Costa, Colombia

James C. Hower
University of Kentucky, james.hower@uky.edu

Erika Blanco
Universidad de la Costa, Colombia

Marcos Leandro Silva Oliveira
Universidad de la Costa, Colombia

Suzi Huff Theodoro
Área Universitária, Brazil

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Research Paper

Possibilities of using silicate rock powder: An overview

Claudete Gindri Ramos [a,*], James C. Hower [c,d], Erika Blanco [a], Marcos Leandro Silva Oliveira [a,b], Suzi Huff Theodoro [e]

[a] Department of Civil and Environmental Engineering, Universidad de la Costa, Calle 58 #55-66, Barranquilla, Colombia
[b] Departamento de Ingeniería Civil y Arquitectura, Universidad de Lima, Avenida Javier Prado Este 4600, Santiago de Surco 1503, Peru
[c] Center for Applied Energy Research, University of Kentucky, 2540 Research Park Drive, Lexington, KY 40511, USA
[d] Department of Earth & Environmental Sciences, University of Kentucky, Lexington, KY 40511, USA
[e] Postgraduate Program of Environment and Rural Development (PPG-MADER), Área Universitária, 01, Vila Nossa Senhora de Fátima – Campus UnB, Planaltina, DF, Brazil

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ABSTRACT

This study evaluates the on use of crushed rocks (remineralizers) to increase soil fertility levels and which contributed to increase agricultural productivity, recovery of degraded areas, decontamination of water, and carbon sequestration. The use of these geological materials is part of the assumptions of rock technology and, indirectly, facilitates the achievement of sustainable development goals related to soil management, climate change, and the preservation of water resources. Research over the past 50 years on silicate rocks focused on soil fertility management and agricultural productivity. More recently, the combined use with microorganisms and organic correctives have shown positive results to mitigate soil degradation; to expand carbon sequestration and storage; and to contribute to the adsorption of contaminants from water and soil. In this article we show results obtained in several countries and we show that this technology can contribute to the sustainability of agriculture, as well as to reverse global warming. Although mineral nutrients are released more slowly from these types of inputs, they remain in the soil for a longer time, stimulating the soil biota. In addition, they are a technology to soluble synthetic fertilizers replace, since the few nutrients derived from such inputs not consumed by plants are lost by leaching, contaminating groundwater and water resources. In addition, conventional methods rely heavily on chemical pesticides which cause damage to soil's microfauna (responsible for the decomposition of organic matter and nutrient cycling) and the loss of organic carbon (in the form of dioxide), which is quickly dispersed in the atmosphere. Silicate rock powders are applied *in natura*, have long-lasting residual effects and reduce greenhouse gas emissions.

1. Introduction

Some types of rocks provide the nutrients required for the full growth of plants, for a period of up to five years after their incorporation into the soil (Theodoro and Leonardos, 2006; Theodoro et al., 2013). As plants absorb only what they need for their development, the other nutrients are retained in the crystalline structure of the minerals (or clays) that make up the rocks added to the soil, forming a kind of nutrient bank, which will be made available in subsequent crops. This fact is extremely relevant both from an economic point of view (costs diluted over time) and environmental (no contamination or pollution of natural resources - soil, water, and air) (Islam et al., 2019; Morillas et al., 2019; Pigatto et al., 2020; Zamberlan et al., 2020; Streit et al., 2021).

The use of stone meal technology by farmers is facilitated by the simplicity of their assumptions, the results obtained in terms of productivity and the low costs, since there is a wide availability of rocks (or their by-products) suitable for this use (basalts, shales, phonolites, kamafugites, etc.). In general, the silicate rocks that have been used in various studies are natural sources of phosphorus, potassium, calcium, and magnesium, in addition to a series of micronutrients that are essential for plant nutrition. The great potential use of crushed rocks as a soil remineralizer lends itself to other purposes, such as the recovery of degraded areas, as adsorption of contaminants in water, and as an inducer of carbon sequestration processes atmospheric.

The high level of contaminants as potentially toxic elements (PTEs) in water is a matter of increasing concern worldwide (Ruggieri et al., 2008; Saikia et al., 2018; Akinyemi et al., 2019; Gasparotto et al., 2019; Gredilla et al., 2019; Ramírez et al., 2019). Various treatment processes for removing contaminants from water include adsorption, coprecipitation, membrane filtration, and electrocoagulation. Adsorption is a low-cost, simple and viable technology for small-scale application (Bissen and Frimmel, 2003). Research on the use of low-cost alternative sorbents such as silicate rocks bearing zeolites (natural zeolites) to remove contaminants from water has intensified (Faghihian

* Corresponding author at: Department of Civil and Environmental Engineering, Universidad de la Costa, Calle 58 #55-66, Barranquilla, Colombia.
E-mail address: cgindri@cuc.edu.co (C.G. Ramos).

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and Bowman, 2005; Ruggieri et al., 2008; Inglezakis et al., 2010; Margeta et al., 2013; Jakkula and Wani, 2018; Lim et al., 2019).

Another interesting finding of this review is the clear influence of enhanced weathering of rocks on the sequestration CO_2. Increasing concentrations of CO_2 in the atmosphere and other greenhouse gases emitted by human activities have left scientists apprehensive about the possible climatic consequences. Humans live in a small subset of climates to be had on Earth, characterized by common annual temperatures around ~13 °C (Xu et al., 2020); a distribution likely reflecting a temperature range of interest associated with essential constraints. The authors additionally note that, with the combination of populace boom and global warming, within the next 50 years it is projected that up to 3 billion people might at risk from extreme climates. Climate change affects the current environmental balance established on the planet, supposedly damaging the balance established between the oceans and biosphere, thus threatening global food security (Rosenzweig et al., 2014). Under normal concentrations the CO_2 is a primary factor from two points of view: plant metabolism and global climate balance.

The concern is that these changes are taking place at a time of increase in the demand for food associated with the growing world population, which may reach 9 billion in 2050, with agriculture contributing significantly to climate change (Godfray et al., 2010; Saikia et al., 2014, 2015; Duarte et al., 2019; Ferrari et al., 2019; Ramos et al., 2019; Cortés et al., 2020; Madureira et al., 2020).

Agricultural crops are increasingly compromised by the loss of the arable layer of the soil at rates exceeding its natural formation rates and by the depletion of essential nutrients such as phosphorus (P) and potassium (K) (Amundson et al., 2015). Soil fertilization is usually carried out with high solubility fertilizers, which are produced at a high cost with finite natural resources (Amundson et al., 2015).

The aim of this work is to present the possibilities related to the use of silicate rocks power and their advances and challenges. The results reported here are derived from a series of studies carried out by researchers from several countries.

2. Soil remineralizing

The global population will require a supply of sufficient and good quality food and water (Gredilla et al., 2017; Nordin et al., 2018). By 2050, food production will increase 70% worldwide and 100% in developing countries. The quantity and nutritional quality of food contribute to human health (Civeira et al., 2016a; Rodriguez-Iruretagoiena et al., 2016). Ninety-five percent of food production depends on the soil, but only healthy soils can provide the necessary ecosystem services and ensure the supply of food and fiber (FAO, 2009).

The characteristics presented by the incorporation rock powder into soil (soil remineralizer) which consists of the addition of macro- and micronutrients to the soil by the application of ground rocks and incorporate several principles of agroecology, since they do not have an exclusive focus on production, but also on the ecological and socioeconomic sustainability of the production system (Theodoro and Leonardos, 2006). This technology has been used for a long time and its results are shown in Brazil (Theodoro and Leonardos, 2014) and other countries, such as Uganda and South Africa (Van Straaten, 2002, 2006), Sri Lanka (Weerasuriya et al., 1993), Norway (Bakken et al., 1997), and Germany (Hildebrand and Schack-Kirchner, 2000). In general, these geological materials present chemical and mineralogical compositions that, when added to the soils in adequate quantities, can amplify the remineralization process (Ramos et al., 2014, 2015).

In the 1970s and 1980s, some studies were carried out in Brazil in which rocks were used to supply K and other nutrients to the plants as part of a search for alternatives to potassium fertilizers and attempting to develop physical and chemical processes for the treatment of Brazilian rocks with higher K levels.

In a rural settlement in the state of Minas Gerais, Theodoro and Leonardos (2006) conducted an agricultural experiment where he compared the productive results for several crops (corn, beans, sugarcane, cassava, among others) using ground-rock potassium with conventional fertilization (NPK) and organic fertilization. The results revealed that there were significant changes in soil fertility levels over five years. In addition, other results show that: (a) the productivity in the plots fertilized with rock powder was equal to or greater (up to 40%) than the plots where chemical fertilizer was used; (b) long-term crops (sugarcane and cassava) achieved better yields; (c) corn and rice also increased productivity, reaching the levels of the areas treated with chemical fertilizers; (d) the additional use of organic compounds was advantageous, showing that the combination of organic fertilizers and rock powder can meet most or even all nutritional requirements of macro and micronutrients; (e) higher humidity was observed in the plants fertilized with the rock powder, demonstrating that the clay content of the material has water retention capacity; (f) plants fertilized with rock powder showed more lush green leaves (cassava and sugarcane); (g) roots of plants treated with rock powder showed a better development compared to the control; and (h) costs of application of rock powder were much lower (<60%), with long-term effects on fertility.

Silva et al. (2008), studying the effects of remineralizers and organic residues on chemical attributes of a subsoil exposed on the growth of *Astronium fraxinifolium*, applied four doses of basalt (0, 2, 4, and 8 t ha^{-1}), combined or not with 8 t ha^{-1} of three organic residues (water hyacinth, corral manure, and domestic sludge). The fresh and dry matter of the aerial part and roots of the plants were evaluated at 120 days after the installation of the experiment, as well as soil analysis. When the treatments were compared to the soil control, only the K levels of the water-plus-basalt and manure-plus-basalt treatments and the P content of the sewage sludge-plus-basalt treatment were higher than those of the control and were generally observed the increase of nutrient contents with the amount of basalt applied.

The agronomic efficiency of the remineralizers is directly related to their mineralogy and chemistry, as well as to the characteristics of the soil that will receive the ground rocks (organic matter content, pH, and texture), crop types, and other environmental and management factors. The main challenge in the use of rocks as fertilizers is in the optimization of the solubility of these rocks, for example, by increasing the surface of the mineral by means of its comminution (Van Straaten, 2007). In tropical regions, due to climatic conditions (high temperatures and rainfall) as well as to the action of plants and microorganisms (through organic chemical reactions in the mineral), weathering processes are favored. In this aspect, several types of rocks may be suitable for use as fertilizers or soil correctors (Manning and Theodoro, 2020).

Leonardos and Theodoro (1999) showed the results of a comparative study on the effects of using ground meal rock (stone meal), soluble fertilizers (NPK) and the mixture of both for the growth of eucalyptus trees over more than 10 years. According to the authors, initially the trees fertilized with NPK and with crushed rock + NPK showed better germination and growth results. But after the third year, there was an inversion and the plots that contained only rock dust and the mixture showed plant growth results superior to those fertilized only with NPK. At the end, trees that received only NPK showed growth rates lower than those that received crushed rocks with or without mixture. Theodoro and Leonardos (2006) suggested that mixtures of NPK with crushed rocks could become a transition mechanism from the conventional model to a more sustainable production model. According to Theodoro and Leonardos (2006), soluble fertilizers would supply the initial need for macronutrients for plants, which would later be supplied by the wide diversity of macro and micronutrients available in the minerals that form silicate rocks (Fig. 1).

Burbano and Theodoro et al. (2020) compared the development of quinoa plants according to five types of treatments (basaltic rocks (R), NPK, organic compound (OC), the mixture of basaltic rocks + organic compound (R + OC), and the control plots). They used the same type

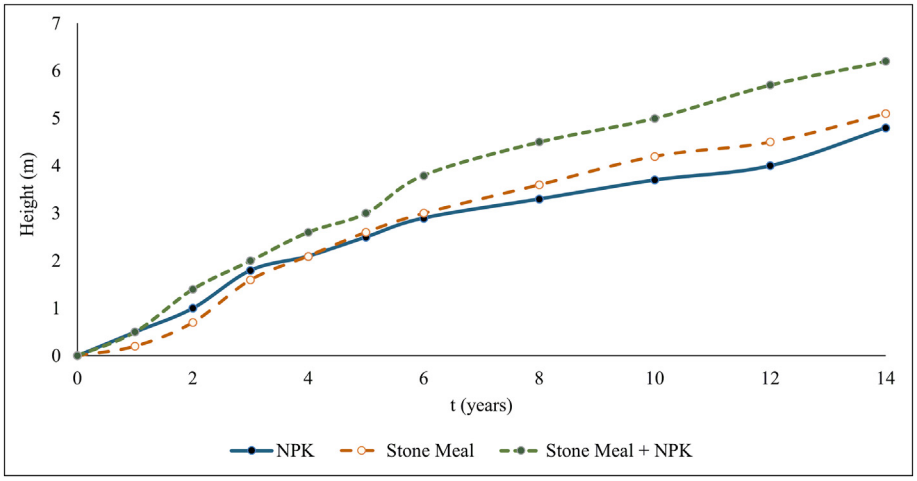

Fig. 1. Basaltic stone meal effect based on the growth of eucalyptus trees (modified from Leonardos and Theodoro, 1999).

of soil (oxisoles) and a basaltic rock of similar composition to that used by Leonardos and Theodoro (1999), however the most recent study was conducted for crops of short cycle (beans, arugula, and quinoa) in rotation system. The results were similar to those obtained in the Leonardos and Theodoro (1999) study. The first two crops (beans and arugula) showed more significant productive results in the plots fertilized with NPK. However, for the third crop (quinoa) there was an inversion and the various indicators analyzed (dry weight of organic matter and productivity) were better in the plots where rock powder (remineralizer) was added mixed with the organic compost (Table 1).

The remineralization of soils is the main assumption of stone meal technology and if they are available locally or regionally, their costs are lower, which will reduce application costs (Van Straaten, 2007) as well as the impacts generated by the excessive consumption of such fertilizers.

In this context, Brazilian law n° 12,890/2013 included remineralizers as an input category for agriculture for a way of making domestic and external market requirements compatible with aspects related to the safety of inputs, regulating the production and use of fertilizers in order to preserve the environment (Brazil, 2013). The Normative Instruction (NI) n° 05 of Ministry of Agriculture, Livestock, and Supply (MAPA), published on March 10, 2016, establish the minimum specifications, and guarantees that must be proven by geochemical and mineralogical analyses, such as sum of bases (K-, Ca-, and Mg-oxides) and maximum percentages of potentially toxic elements. Other aspects considered in NI n° 05 refer to the pH of abrasion, free silica content (quartz), and the granulometry of the materials to be marketed (Brazil, 2016).

Table 1
Comparison of the extrapolated means (in g) for ton per hectare of the organic compound treatments.

Treatments		Bean	Arugula		Quinoa	
		BG	FM	DM	QG	DM
T0	Control (C)	0.96	4.44	0.83	0.46	5.04
T1	Organic Compost (OC)	2.46	7.17	1.17	0.66	5.71
T2	NPK	3.96	9.19	1.33	0.91	7.62
T3	Remineralizer (R)	1.12	6.34	1.25	1.12	7.62
T4	R + OC	2.71	7.27	1.29	1.29	7.66

Source: Burbano et al. (2020).
NPK: chemical fertilizer; R: remineralizer; R + OC: remineralizer + organic compound; C: control; BG: Bean grain; FM: Arugula fresh matter; DM: Arugula dry matter. GR: Quinoa grain; MS: Dry matter.

Rock powders have been reported as a soil remineralizer and a source of plant nutrients in several countries such as Australia and India (Basak, 2019; Basak et al., 2020), Brazil (Ramos et al., 2019; Dalmora et al., 2020a), and the United Kingdom (Mohammed et al., 2014; Manning, 2018). Theodoro and Leonardos (2006) showed that the rock powder application blended with organic by-product achieved better productivity crop yields than the sole application of rock powder. The combined application of dacite powder with organic-matter can be a promising approach because insoluble nutrients in mineral rocks can be to available forms by the action of organic acids produced during organic-matter decomposition (Basak et al., 2017). This characteristic may be advantageous for the blended with other less bioactive by-product, but with a larger nutrient diversity, such as dacite rock powder (Ferrari et al., 2019; Firpo et al., 2021). These point to the possibility of converting by-products with contamination environmental potential in inputs to be used in agriculture.

The characterization research of volcanic rock by-products for use as soil fertilizer for soils should include, besides macro and micronutrients, the evaluation of potentially toxic elements presents in these materials. Some are essential to plants, while others are toxic elements, which, if made available to the soil, may affect the environment and human health (Gasparotto and Martinello, 2021).

In the studies by Ramos et al. (2015, 2017) with acid volcanic rock and different extractive solutions, it was verified that in the leachates, even at extremely acidic pH, the elements of high toxicity like As, Cd, U, among others, presented low bioavailability. There was no significant transfer of Al, Cd, Fe, Ni, Pb, and Zn to the leachate from the rocks tested (Dias et al., 2014; Rodriguez-Iruretagoiena et al., 2015; León-Mejía et al., 2016, 2018; De Vallejuelo et al., 2017).

Ramos et al. (2019) performed a detailed granulometric, petrographic, chemical, and mineralogical characterization of the dacite rock powder, and its potential use as soil remineralizer also to in black oats and, sequentially, maize crops. The study stands out for its contribution to the mitigation of by-product production since it is the first study to reuse these by-products as a soil fertilizer. Fig. 2 shows a comparison between black oats and maize crops growth cultivated with a dacite powder dose of 7251 kg ha^{-1} and without dacite rock powder.

The determination of the agronomic efficiency index and the quantification of the residual effect of nutrients contained in the rocks are prerequisites to the correct sizing of the recommendations of fertilization with the rocks, aiming at the recovery and maintenance of the soil fertility and its nutritional balance, in production systems. Therefore, this type of evaluation should be carried out under the most varied experimental conditions in no-tillage systems, crop-livestock

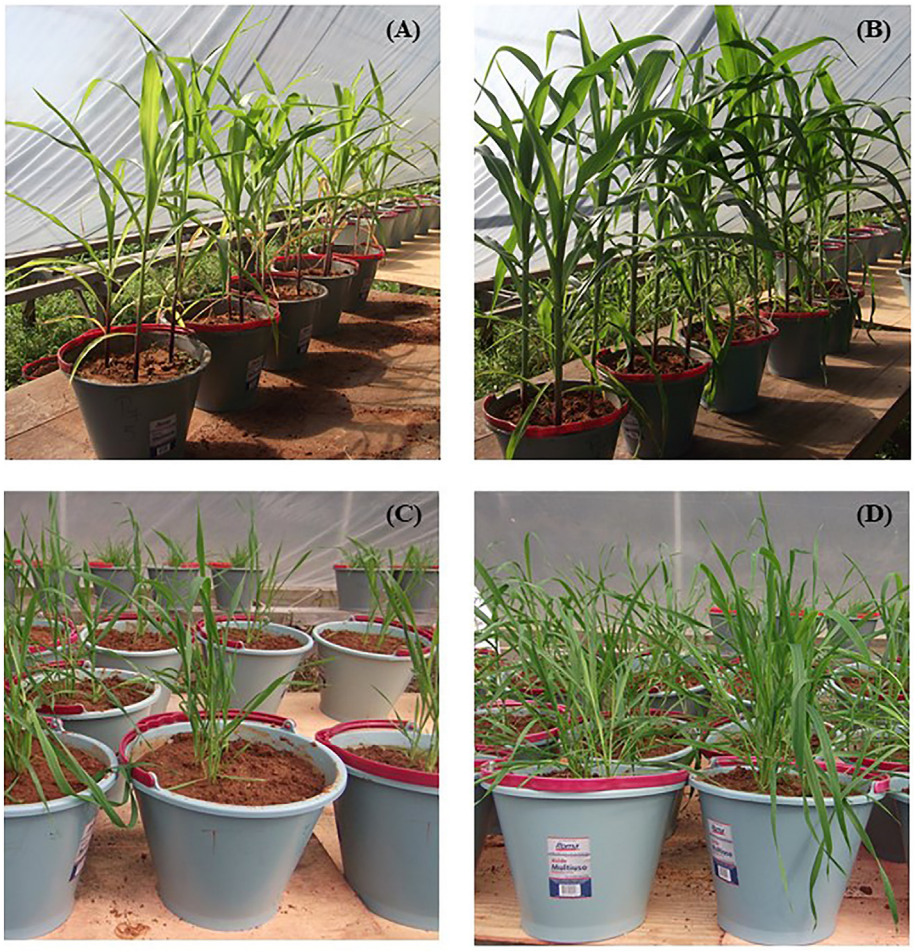

Fig. 2. Comparison between black oats (A, B) and maize growth (C, D), cultivated with and without silicate rock powder, respectively.

integration, fruit-growing, and silviculture integration, and also in consideration of conventional and organic production modalities (Abbott and Manning, 2015).

Given the complex nature of rocks and minerals, appropriate analytical procedures need to be defined to satisfactorily characterize the composition and bioavailability of existing rock elements, as crop responses may be associated not only with K from rocks, but to conjugated factors and effects arising from its composition (Ramos et al., 2017).

The chemical and mineralogical compositions of rock powder required by NI n° 05 (Brazil, 2016) can be obtained by analytical techniques such as X-ray fluorescence (XRF), to determine the largest elements in % of the weight of the oxides (Gómez et al., 2021; Nieves et al., 2021; Rautenbach et al., 2021; Sumbane-Prinsloo et al., 2021).

The results of the analysis provide the parameters of the Sum of Bases ($CaO + MgO + K_2O$), the K_2O content, in addition to other compounds of agricultural interest. Inductively Coupled Plasma Spectroscopy (ICP) is the most suitable technique to determine the concentrations of toxic elements (As, Ca, Hg, and Pb), macro and micronutrients. The analysis method consists of digesting 10 g of rock powder sample, in a hot extract of HNO_3 followed by HF: HNO_3: $HClO_4$ (Querol et al., 1997). The results are determined by Inductively Coupled Plasma - Atomic Emission Spectrometry (ICP-AES) and Inductively Coupled Plasma - Mass Spectrometry (ICP-MS). The semi quantitative determination of the mineral phases constituting the rock is performed by X-ray diffraction (XRD) (Oliveira et al., 2018, 2019a; Akinyemi et al., 2021). Generally, the XRD analytical technique uses an angular range of 3° to 70° 2θ in a step of 0.05°/2 s using divergence and 1° and 0.2 mm anti-scattering slits in the detector.

In addition to the assessment of the mineralogical and chemical characterization of the rock established in NI n° 5/2016, many authors (Theodoro and Almeida, 2013; Ramos et al., 2014, 2015, 2017; Dalmora et al., 2020a, 2020b; Ribeiro and Flores, 2021) perform tests of leaching to assess the release of macro, micronutrients, and potentially toxic elements in a 2% citric acid solution and in deionized water. The acid extraction method has been widely used to assess the availability of nutrients in different rocks. Digestion with 2% citric acid solution is one of the methods for determining phosphorus in fertilizer samples in Brazil (Brazil, 2014). This method consists of transferring exactly 1.0 g of the rock dust sample to a 250-mL conical flask, adding exactly 100 mL of the citric acid solution, followed by stirring between 30 and 40 rpm for 30 min, and subsequent filtration to the chemical determination of the filtrate. The leaching test, based on the European standard (EN 12457–2, 2002), uses a ratio of 1:10 (weight/volume), in which 1 g of powder sample is weighed in a 15-mL Falcon tube and added 10 mL of deionized water, with stirring at 30 rpm for 24 h. It is desirable that the filtered leachate be analyzed by ICP spectroscopy.

Theodoro et al. (2020) carried out a research using remineralizers and organic compost to recover a degraded area in a conservation unit, in the Brazilian Cerrado region. To assess the beneficial effect of remineralizers over time, an agroforestry system was implemented, using seven types of treatments, which included remineralizers (derived from kamafugites); sediments retained in a large reservoir, organic compound (manure) and mixtures of these inputs, in addition to control plots. Germination and development of six forest species (all native to the region) were monitored over seven years. Among the results of the research, the authors mention that there was an

increase in fertility levels and soil structure in the plots that received organic compost + remineralizers = sediments. Trees also took advantage of the greater supply of nutrients derived from geological sources and showed the highest growth rates in these plots.

According to Bergmann et al. (2013), the basaltic spills from the Serra Geral Group in Brazil are composed of, aside from silicate minerals, zeolites and clay minerals in the top zone or in the form of spills of the lobules type. These minerals are used in industrial, livestock, agriculture, and aquaculture production systems, due to their high cation exchange capacity, and the potential for adsorbing gases and vapors due to crystalline structure. Within the possibilities of agronomic use, zeolites have adsorbent properties of ions and molecules that represent sources of nutrients for plants. Essential nutrients such as K, Ca, and Mg, besides to nitrogen compounds which are highly volatile, can be retained in the pore and canaliculus systems from zeolites, becoming available to plant roots (Shinzato et al., 2010).

3. Adsorption of contaminants in effluent

Zeolites are hydrated aluminosilicates of alkali and alkaline earth metals belonging to the mineral class of tectosilicates. Zeolites consist of a three-dimensional structure of SiO_4 and AlO_4 tetrahedra (Ruggieri et al., 2008). The negative charge of the zeolite structure is defined by substitution of Al for Si, which is compensated by cations of alkali and alkaline earth metals. Natural zeolites are cation exchangers due to having a negative charge on the surface. In the zeolite crystalline network, the substitution is not limited to the replacement of Si—Al. Si can also be replaced by atoms like Fe, Bo, Cr, Ge, and Ti (Margeta et al., 2013). The substitution of Si and Al in zeolites varies from a minimum ratio of 1: 5 (mordenite) to a maximum of 1: 1 (erionite) (Breck, 1974).

The exchangeable cations such as Na, K, Ca, and Mg are particularly suitable for the removal of undesirable contaminants, such as water PTEs (Vaca-Mier et al., 2001). The adsorbent substances present significant variations in their adsorption capacities and, due to this variation, there is considerable interest in the study of zeolites. Zeolites are the most important inorganic cation exchangers because they are solids capable of immobilizing certain components of a fluid phase on their surface. According to Lim et al. (2019) a good representation of these characteristics is found in zeolitic adsorbents. Several studies (Haggerty and Bowman, 1994; Faghihian and Bowman, 2005; Walcarius et al., 2006; Campos, 2009; Inglezakis et al., 2010) reported that the adsorption processes with zeolites encompass a dynamic and promising research field because these substances are crystalline and microporous and because of this they present numerous advantages over conventional solid adsorbents.

According to Dabrowski (2001), activated carbon and zeolites are the most representative porous solids. The porous network that constitutes zeolites is responsible for their high internal surface, so that the ordered crystalline structure gives uniformity to the dimensions of their pores, and for this reason, they are able to select the molecules that, due to their shape and size, may have matrix access. Due to the presence of aluminum in their structure, some zeolites have strong acidic sites that make them a potential catalyst. What distinguishes zeolites from other porous substances such as activated carbon and alumina, for example, is the size of the pores that prevent larger molecules from penetrating into them (Dabrowski, 2001).

Scanning electron microscopy (SEM) is a suitable technique for determining the structure, pore size and chemical composition of zeolites. These parameters are essential for an adequate understanding of the adsorption properties of these materials (Jentys and Lercher, 2001; Ribeiro et al., 2010, 2013a, 2013b; Quispe et al., 2012; Ramos et al., 2015, 2017). The electron-sample interactions that occur during SEM analysis, reveal information about the nature of the analyzed material, including composition, topography, electrostatic potential, local magnetic field, among other properties (Civeira et al., 2016b; Oliveira et al., 2018; Hower and Groppo, 2021). SEM analysis accompanied by dispersive energy detectors (EDX) makes it possible to identify the chemical composition of the samples (Oliveira et al., 2019a, 2019b, 2019c, 2019d, 2020). Several researchers (Inglezakis et al., 2002; Inglezakis and Grigoropoulou, 2003; Cutruneo et al., 2014; Sánchez-Peña et al., 2018) used SEM/EDX analysis to obtain the chemical composition of minerals, as well as their structures through microphotographs.

X-ray diffraction is a technique used to identify the mineral phases that make up a material. The intensities measured with XRD can provide semi-quantitative information on the phase composition present in the crystalline structure (Brundle et al., 1992). X-ray diffraction analyzes have been commonly used by several authors (Dyer and Zubair, 1998; Bosso and Enzweiler, 2002; Christidis et al., 2003; Dalmora et al., 2016; Dutta et al., 2017, 2020) to characterize mineral.

Many natural adsorbents may have high ion exchange capacity for some ions, but they may also have reduced capacity or no adsorption capacity for some functional groups. The modifications of these materials provide significant advances in the adsorption capacity, so that the adsorbent materials can be enriched with certain ions in order to establish chemical bonds with other ions present in the fluid (effluent) when in contact with the solid.

Several researchers (Haggerty and Bowman, 1994; Faghihian and Bowman, 2005; Walcarius et al., 2006) carried out studies with the objective of improving the adsorption capacity through modifications of adsorbent substances. The treatment of polluted and/or contaminated liquid effluents is usually carried out through a step of physical adequacy of the waste and, another, which involves specific methods of removing cations and anions present in the effluent. Several studies show the potential for using natural zeolites as a low-cost contaminant adsorbent material (Fig. 3). According to Kesraoui-Ouki et al. (1994), the applications of zeolites in the control of industrial pollution have become important and the level of technical efforts is increasing. The wide application of zeolites is reported not only for its low cost, but also for obtaining excellent properties and adsorption characteristics that enable the implementation of natural zeolites in the adsorption of contaminants from liquid effluents.

According to Bergmann et al. (2013) zeolites are used in industrial production systems, livestock, agriculture, and as a way to control and mitigate the emission of pollutants, even leading to the production of high-cost synthetic, designed for specific uses. Concentration and use technologies are defined for the most common varieties in these environments, such as clinoptilolite, mordenite, heulandite, and analcime. The occurrence of zeolites in cavities in volcanic rocks has been reported since the 1950s (Bergmann et al., 2013).

Campos (2009) investigated the natural zeolite (mordenite) from the Serra Geral Group, western portion of the State of São Paulo, Brazil, as adsorbent material from As, Cr, Pb, and Mn from Lago Carapicui, Brazil. The results of the author revealed that the zeolite (without any previous treatment) removed 78.7% of Pb and 19.6% of Mn from the lake water at pH values <6.

Inglezakis et al. (2010) used clinoptilolite to remove Fe and Mn from groundwater samples from the Attica region, Greece. The results showed that the zeolite removed 61% of Fe and 100% of Mn, reaching the maximum permitted concentrations according to the environmental legislation in force in the European Union.

When nuclear accidents occurred at Three Mile Island (Pennsylvania) and Chernobyl (Ukraine), natural zeolites (clinoptilolite) were applied to remove the radioactive isotopes Cs and Sr from the effluents of the nuclear industry (Rivera et al., 1998) and to decontaminate the water. Natural clinoptilolite zeolite was also applied at the Sellafield Ion Exchange Effluent Plant (United Kingdom), which reduced discharges of ^{137}Cs and ^{90}Sr in the Irish Sea to relatively constant levels, and significantly improved the radioactive conditions of the studied area (Lam et al., 1998).

Studies with significant results in the removal of ammoniacal nitrogen, heavy metals, organic compounds, and radioactive elements using

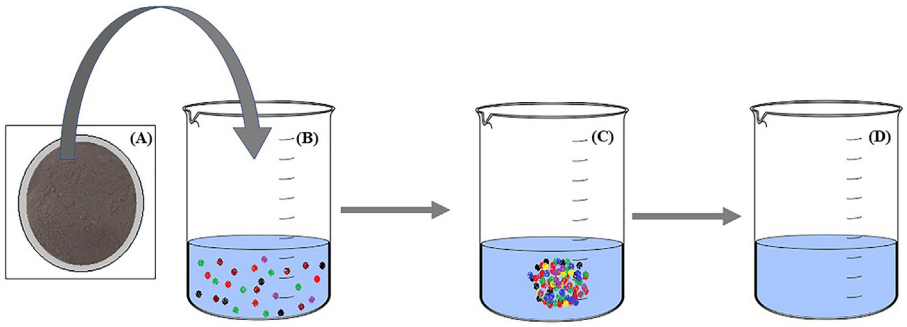

Fig. 3. Summary of the water contaminant adsorption system. (A) Silicate rock powder; (B) Contaminated water; (C) Adsorption of contaminants; (D) Decontaminated water.

zeolites can be observed in the literature (Arenas-Lago et al., 2014a, 2014b).

Duarte et al. (2002) mentioned the use of natural stylbite zeolite (STI-NAT) from the Parnaíba Basin, Brazil in the treatment of effluents containing 500 mg L^{-1} of lead and copper. These authors performed the treatment of zeolite with 2 mg L^{-1} NaCl (STI-NaCl) and 0.5 mg L^{-1} NaOH (STI-NaOH) showed an improvement of 68%, 97%, and 99.9% for STI-NAT, STI-NaCl, STI-NaOH, respectively, in the removal of lead heavy metal, while for copper metal there was a 21% removal for STI-NAT, 31% STINaCl, and 96% STI-NaOH.

The study by Jimenez et al. (2004) highlighted that the use of scolecite with a particle size less than 0.074 mm in aqueous effluents showed a high adsorption power in the removal of Cr^{3+}. Shinzato et al. (2009) studied the removal of Pb^{2+} and Cr^{3+} with the use of modernite zeolites that make up the amygdaloid dacites found in the region of Timburi, Sao Paulo, Brazil. The results of the adsorption tests showed that the samples of modernite showed an efficiency in the removal of 98.18% for Pb^{2+} and 19.34% for Cr^{3+}.

Fialho et al. (2018) evaluated the efficiency of ammoniacal nitrogen adsorption using aggregate of horizons of amygdaloid volcanic rock filled with zeolites from a quarry in the municipality of Estância Velha, in the state of Rio Grande do Sul. The study consisted of treating a solution prepared with chloride ammonium (PA) of 50 mg L^{-1}. The results indicated an efficiency in the removal of 99.95% of ammoniacal nitrogen.

Bosso and Enzweiler (2002) verified a greater affinity of scolecite in removing Cu^{2+}, Pb^{2+}, and Zn^{2+} from aqueous solutions compared to Ni^{2+}, Co^{2+}, and Cd^{2+}. The cation for which scolecite showed greater removal efficiency was Pb^{2+}, which in a solution with an initial concentration of 30 mg L^{-1}, at pH 6, adsorbed approximately 5.8 mg g^{-1}. In another study using scolecite, in which Cr^{3+}, Ni^{2+}, Cd^{2+}, and Mn^{2+} cations were investigated, the highest adsorption efficiency occurred for Cr^{3+}. For this cation, complete removal of a 50 mg L^{-1} initial concentration solution was observed (Cerqueira et al., 2011, 2012; Martinello et al., 2014; Morillas et al., 2018a, 2018b).

Alvarez-Ayuso et al. (2003), in their studies on chromium removal from aqueous solutions using clinoptilolite, demonstrated the removal of 91% of total Cr from a solution containing 100 mg L^{-1} of Cr.

Basaldella et al. (2007) evaluated the possibility of removing Cr^{3+} from aqueous solution by applying a synthetic zeolite, NaA, and, using 1 g of zeolite, obtained almost complete removal of the cation present in 1 L of 42 mg L^{-1} concentration solution.

Lim et al. (2019) performed adsorption test to evaluate clinoptilolite zeolite and zeolite with feldspar as a Cu, Cd, and Pb adsorbent in contaminated groundwater. The results obtained by Lim et al. (2019) showed that the adsorption of Cu, Cd, and Pb ions were 145.84 mg g^{-1}, 177.99 mg g^{-1}, and 802.23 mg g^{-1}, respectively, by clinoptilolite zeolite, and 154.71 mg g^{-1}, 162.58 mg g^{-1}, and 932.08 mg g^{-1}, respectively, by zeolite with feldspar. The authors concluded that the both absorbents have excellent removal efficiency of Cu, Cd and Pb ions in contaminated groundwater.

4. Carbon sequestration

It is undeniable that measures to control climate change are necessary, since the average temperature on land and the ocean surface in 2016, the third consecutive year of global warming records, was the highest since 1880. According to the National Oceanic and Atmospheric Administration (NOAA), in its annual report on global climate, the average global temperature across land and ocean surface areas for 2016 was 0.94 °C above the 20th century average of 13.9 °C, surpassing the previous record warmth of 2015 by 0.04 °C. Global temperatures in 2016 were mainly influenced by the El Niño phenomenon that prevailed at the beginning of the year (NOAA, 2016, 2019). Since the beginning of the 21st century, the annual global temperature record has increased five times in the years 2005, 2010, 2014, 2015, and 2016 (NOAA, 2017). The year 2019 turned into the second warmest year in the 140-year record, with a worldwide land and ocean surface temperature departure from normal of +0.95 °C. This rate is only 0.04 °C lower than the record rate of +0.99 °C established in 2016 and 0.02 °C higher than +0.93 °C established in 2015. Nine of the 10 warmest years in the 1880–2019 period have happened since 2005, with 1998 presently ranking as the 10th warmest year on record. The year 2019 marks the 43rd consecutive year, dating to 1977, in which worldwide land and ocean temperatures, as a minimum nominally, have exceeded the 20th-century normal. It may be vital to stabilize the concentrations of greenhouse gases in the ecosystem at a stage that prevents risky anthropic interference with the weather system (Schneider et al., 2015, 2016; Sehn et al., 2016; NOAA, 2019; Pacitto et al., 2020; Rojas et al., 2019). That stage needs to be reached in enough time to permit ecosystems to evolve to the weather change, making sure that food production is not threatened and permitting economic improvement to continue in a sustainable manner (Lee et al., 2015).

Hansen et al. (2017) estimated a global warming rate of 0.18 °C per decade. The global average temperature has already exceeded 1 °C of the pre-industrial level and will possibly exceed the limit of 1.5 °C established by the Paris Agreement of the United Nations (UNFCCC, 2015) in the next 30 years. In order to contemplate global climate goals, coincident with the reduction of CO_2 emissions from fossil fuels, alternative measures of CO_2 sequestration on a large scale are necessary (UNEP, 2018).

When CO_2 reacts with Ca and Mg cations, which are present in abundance of silicate minerals such as olivine, serpentine, wollastonite, and Ca-plagioclase, it configures itself in a favorable process to form carbonate minerals. The natural weathering and the chemical and physical alteration of minerals favors the formation of carbonate by breaking the structure of the silicate and releasing Ca and Mg. It even promotes mineral carbonation, through dissolution and hydrolysis leading to the fixation of CO_2 in bicarbonate or carbonate ions in solution (Wilcox, 2012). Due to natural weathering limiting the process of mineral carbonation, several researchers have suggested the possibility of CO_2 sequestration through accelerated weathering (Goff and Lackner, 1998; Rau and Caldeira, 1999; House et al., 2006). According to Hartmann

et al. (2013), the kinetics of weathering of silicate rocks can be increased through actions such as comminution of mineral particles to increase the mineral surface area; by changing the pH of the reagent solutions; by the increase in temperature; in pressure; the choice of rocks with highly reactive minerals; by changing the flow regime; and using biological materials. The latter authors point out that making combined use of some of these actions is a strategy for accelerated weathering. A comparison of dissolution rate constants of some silicate minerals is shown in Fig. 4.

According to UN (2015), a strategic measure of CO_2 sequestration that includes several UN Sustainable Development Goals is the improved weathering of rocks. Amann et al. (2020) proposed to enhance this process by actively capture CO_2 from the atmosphere. Accelerated weathering is a process that accelerates the natural reaction between CO_2 and reactive sources, such as certain types of rocks, to increase carbon absorption. IPCC (2014) estimated that its removal potential is 0.5 to 4 Gt CO_2 eq. per year. This technology promotes soil improvement through the application of silica rock powder that accelerates the carbon-sequestration process and has the potential to increase agricultural production, protect plants against pests and diseases, and assist in the remineralization of infertile soils (Beerling et al., 2018; Ramos et al., 2019; Dalmora et al., 2020a). The minerals of silicate rocks, when added to the soil, react with the CO_2 present in the rhizosphere, releasing basic cations such as Ca^{2+}, Mg^{2+}, and K^+ and promotes an increase in soil pH values. This reaction, depending on the chemical property of the soil, can form pedogenic carbonates that can be drained into the oceans (Renforth and Henderson, 2017). Both mechanisms store carbon with an estimated useful life of tens of millennia. Improved weathering of rocks, when carried out on a large scale, can be a carbon sequestration strategy with the potential to guarantee food and soil security and prevent ocean acidification (Taylor et al., 2016).

Several authors have evaluated CO_2 removal rates and responses to crop performance and improvements in soil fertility attributes through the application of silicate rock powder (Fig. 5) (Renforth et al., 2015; Ramos et al., 2017, 2019; Amann et al., 2020; Dietzen et al., 2018; Dalmora et al., 2020a, 2020b).

Renforth (2012) carried out a case study on an energy/carbon balance together with the associated operating costs for the United Kingdom. According to the author, silicate sources are large and can theoretically capture 430 Gt of CO_2. Most of this resource is contained in basic rocks that have a carbon-capture capacity of ~0.3 t CO_2^{-1} rock. In contrast, ultra-basic rocks (0.8 t CO_2^{-1} of rock) have a total carbon-capture capacity of 25.4 Gt CO_2. Renforth (2012) additionally indicated that the energy expenses of intensified weathering may be 656–3501 kWh t CO_2^{-1} for basic rocks and 224–748 kWh t CO_2^{-1} for ultra-basic rocks. Comminution and the shipping of substances are the activities that demand more energy, collectively accounting for 77%–94% of energy needs This rate is only 0.04 °C lower than the record rate of +0.99 °C established in 2016 and 0.02 °C higher than +0.93 °C established in 2015. The associated expenses of the stepped forward weathering may be US$ 70–578 t CO_2^{-1} and US$ 24–123 t CO_2^{-1} for basic and ultrabasic rocks, respectively.

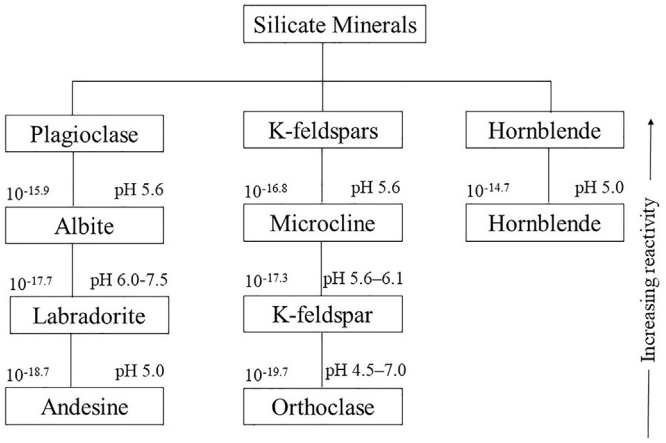

Fig. 4. Variation in dissolution rates for silicate minerals in mol cm^{-2} s^{-1} (from White, 1995).

Direct-flow-dissolution leach-column experiments were performed by Renforth et al. (2015), with analyzes of the elemental composition of the leachate for a period of five months. The results showed the release of Mg from the dissolution of olivine and an estimated dissolution rate of olivine between 10– 16.4 and 10–15.5 mol Mg cm^{-2} s^{-1}. According to the authors, this rate dissolution indicates that it might be essential to grind the olivine to a particle size of 1 μm or less to permit dissolution in 1–5 years, requiring grinding power of approximately 1.5 GJ per ton of rock. The cost would be comparable with the most studied options to CO_2 sequestration, such as direct air capture. On the other hand, the studies by Amann et al. (2020) revealed that the removal of CO_2 due to olivine weathering, the dominant mineral in dunite, is often associated with increases in Ni and Cr, which are potentially toxic to plants and can make their application undesirable as an agricultural input.

Kelland et al. (2020) applied doses of basaltic rock powder equivalent to 10 kg m^{-2} in slightly acidic loamy agricultural soil and cultivated C4 Sorghum to assess the agricultural and carbon sequestration potential through improved weathering of rocks. They demonstrated that the geochemical reactive transport modeling showed CO_2-capture rates of 2–4 t CO_2 ha^{-1} at 1–5 years after only one application of basaltic rock powder. These rates represent a four-times increase in carbon storage compared to plant-soil control systems without basaltic rock powder.

Montserrat et al. (2017) applied the improved weathering in olivine as a large-scale climate engineering approach. In the batch-scale reaction experiments, forsterite was submitted to agitation in different seawater media for periods of days to months. The results showed that forsterite dissolution significantly increased the alkalinity of sea water and the concentration of inorganic carbon due to the invasion of CO_2, thus confirming the viability of the improved silicate weathering. However, the negative principal results of the dissolution of forsterite are an increase in Mg, Si, alkalinity, inorganic carbon, Fe, and Ni, and their consequences at the ecosystems need to be assessed. Increases in dissolved Si and Fe can stimulate primary production and, accordingly, cause extra CO_2 sequestration, as assessed by Hauck et al. (2016).

The sequestration of CO_2 through improved weathering is guided by the principle of acid-base thermodynamics of seawater. This CO_2 will remain dissolved/contained in the sea if there is no change in water alkalinity by other processes. The ocean is an open system and functions as a CO_2 reservoir, allowing the CO_2 to be freely exchanged between the atmosphere and the ocean through the air-sea interface. As leakage is not favored in an open system, CO_2 storage in the ocean is therefore relatively leak-proof. The evidence that CO_2 can be contained for long periods of time is provided by observations of the carbon cycle and the effect of the weathering of the natural silicate; the long-term fate of fossil CO_2 is to be absorbed into the ocean (Archer, 2005).

Dietzen et al. (2018) performed a three-month soil incubation experiment at two rates of application to evaluate the behavior of olivine on the CO_2 flow of the soil, release of Mg and Al, and pH alteration compared to control treatment and lime-corrected soils. The results of this study suggest that olivine is an effective material for carbon sequestration and a suitable alternative to replace the lime. The authors highlighted the potential use of improved weathering as a carbon-sequestration mechanism because, over a short-time, the dissolution of olivine at the lowest application rate would have stored 3.13 t CO_2 ha^{-1}. According to Murray et al. (2005), this quantity is within the range of expected stored rates over a year for a series of common land-management practices for carbon storage, including conservation tillage, changes in pasture management, reforestation, or conversion

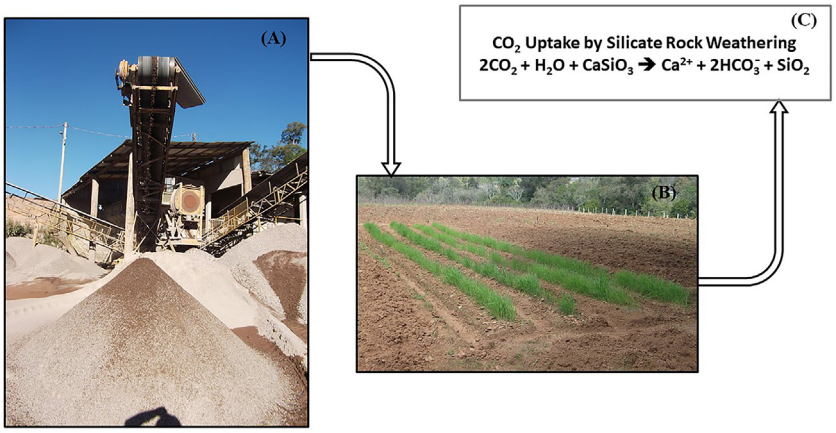

Fig. 5. Summary of the potential effects of weathering of crushed silicate rocks, applied to black oats crop and in CO_2 uptake. (A) Silicate rock powder; (B) Soil remineralization for black oats growth; (C) CO_2 uptake.

of agricultural land to permanent pasture. Dietzen et al. (2018) stated that the use of olivine or other silicate minerals to increase the pH of agricultural soils, instead of lime, would also prevent the emission of CO_2 by liming of soil. Improved weathering has potential to solve the problem of high atmospheric CO_2 concentrations by consuming anthropic CO_2 and reducing agricultural CO_2 emissions (Dietzen et al., 2018).

Abbott and Manning (2015) observed that soil health depends on complex bio-physical and bio-chemical processes interacting in space and time and that combinations of composted organic matter and clay minerals, as zeolites can increase the rate of release of nutrients from rock minerals.

Beerling et al. (2020) applied an integrated performance modeling method to make a preliminary techno-financial assessment for 2050. They quantified CO_2-storage ability and evaluated how expenses range among countries when it comes to energy policies in consideration of a warming of 2 °C. The authors evaluation was primarily based on a one-dimensional model for basaltic rock weathering which took into consideration considered the change in dissolution rates with soil depth and time as the particles dissolve. The simulations performed by Beerling et al. (2020) showed slow and fast kinetics dissolution rates due to different mineral composition of the rocks. Silicate rocks minerals have different kinetic dissolution rates (Ramos et al., 2015, 2017; Dalmora et al., 2020b), with some minerals continuing to dissolve and capture CO_2 after the first year of application (Beerling et al., 2020). The representative calculation of annual carbon sequestration rates requires the calculation of average rates from frequent rock powder applications.

Countries such as China, India, the USA, and Brazil have great potential of rock powder application and can capture 2 Gt of CO_2 each year. According to Taylor et al. (2017), the rock comminution performed to maximize carbon sequestration was the operation that consumed the most energy in the improved weathering. The cost depends on the price of local labor, which ranges from US$ 80 per ton in India to US$ 160 in the United States and is in line with the US$ 100 to US$ 150 carbon price forecast by the World Bank for 2050, the period on which estimated emission to reach net zero to avoid a climatic collapse (Beerling et al., 2020).

The accelerated weathering of rocks can be an attractive option to support the mitigation of climate change, especially in tropical and subtropical regions, where the potential for CO_2 sequestration is the highest. Accelerated weathering is achieved by modifying soils intensively cultivated with rock powder containing Ca and Mg (Schuiling and Krijgsman, 2006; Taylor et al., 2016). This technology has the function of removing CO_2 from the atmosphere, facilitating the rejuvenation of poor or leachate soils, stabilizing the soils organic matter, improving agricultural productivity, conserving geological natural resources, and favoring the marine ecosystem.

5. Future and recommendation

The possibilities for using silicate rock powders are vast. Soil fertilization is simple and can be quickly scaled to the regional level. The rocks are widely distributed and readily available as a cheap by-product. In general, these by-products are abundant in mining plants and are already in crushed and milled form, a fact that does not require new improvement plant and any extra energy to obtain them. The use of rock powder in agriculture is the sustainable way to remineralize soils and can be implemented on a large scale. In tropical countries, with great geodiversity and with an important agricultural sector for the generation of food and income (including participation in the agricultural commodities market), the use of ground rocks (remineralizer or stone meal) becomes an important productive option, especially as these countries are major importers of chemical inputs. Furthermore this innovative method may contribute to the increase of CO_2 sequestration in our soils, as it adds a potential to bring atmospheric carbon to pre-industrial revolution levels (Schneider et al., 2015; Wilcox et al., 2015) through the targeted use of the world's agricultural land. In addition to providing soil revitalization, it can be reduce global CO_2 levels to safe levels and improve water quality parameters without requiring any pretreatment.

Declaration of competing interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

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